

High Pressure Polymerization of Metal Doped C60 ~In an Attempt to Prepare Carbon Clathrate Compounds~

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High Pressure Polymerization of Metal Doped C₆₀ ~In an Attempt to Prepare Carbon Clathrate Compounds~

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Since the discovery of superconductivity in hole-doped diamond [1], much attention has been attracted to synthesis of high T_c superconductors made of carbon covalent networks with controlled carrier concentrations. Diamond is hole-doped by the substitution of the carbon atoms in the framework. If we can have a cage-like sigma bonded network of carbon like that found in silicon clathrate compounds, the carrier doping could be done more efficiently, and more easily.

We have already obtained 3-dimensional (3D) carbon networks with cages by polymerization of C₆₀ crystals under high-pressure and high-temperature (HPHT) conditions (Fig.1) [2]. The 3D C₆₀ polymer can be viewed as clathrate analogs without trapped metal atoms. We would like to intercalate metal atoms into the interstices of the 3D polymer for electron doping. However, it is difficult to dope metal atoms after the hard 3D networks are formed under pressure. In this study, an attempt has been made of preparing metal doped clathrate-like structure utilizing high pressure polymerization of C₆₀ by started from metal doped C₆₀.

Barium doped fulleride monomer crystals Ba₃C₆₀ were treated under HPHT conditions of 5–15 GPa and temperatures up to 1150°C. The resulting products were amorphous solids, which were stable in air. The high micro Vickers hardness comparable to tungsten carbide and the Raman spectra of the solids suggest that the C₆₀ molecules are collapsed to form amorphous 3D-polymer encapsulating Ba atoms. The compound showed a semi-metallic conductivity with a positive Hall coefficient. The electrical properties are comparable to those of a superconducting B-doped diamond. It is likely that barium atoms are trapped in the carbon network, replacing carbon atoms as clusters, and act as dopants for holes, like as depicted in Fig. 2 as the local structure [3].

However, these materials did not show superconductivity, probably due to its small mobility attributed to the absence of translational symmetry of the amorphous sample. It would be necessary to crystallize the 3D-polymers in order to realize high T_c superconductivity.

In recently days, we have found that single crystals of magnesium doped 2D-polymer Mg₂C₆₀ can be directly grown via a binary vapor-phase mixture of Mg and C₆₀ [4]. The structural refinement revealed that a Mg atom is located at each tetrahedral fullerene ball interstice suggesting that the Mg cation is in van der Waals contact with carbon p orbitals.

In this presentation, HPHT treatment and high pressure effect of these single crystals will also be discussed.



Figure 1. Various C₆₀ polymers.

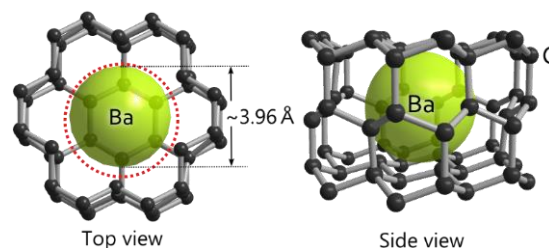


Figure 2. Schematic illustrations of a local arrangement of carbon network encapsulating a Ba atom in Ba₃C₆₀ collapsed by HPHT treatment. The Ba atom (covalent diameter ~3.96 Å) replaces carbon atoms in a six-membered ring with a comparable size. The dotted circle is a covalent diameter (~4.2 Å) of a six-membered carbon ring.

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